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A study of graphitizing coal by X-ray diffraction

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Abstract : The structure of the graphitic carbons is intermediate between the three dimensional crystalline structure of graphite and the randomly distributed lamellae structure of the non-graphitic carbons. In the graphitic carbons, the apparent inter-layer spacing decreases with increasing magnitude of graphitization. X-ray study of Khalaspir coals of Northwestern Bangladesh reveals that these contain small graphitic ring clusters (*i.e.* lamellae of condensed aromatic rings), which becomes more graphite-like as coalification progresses The average separation distance between lamellae becomes smaller as the rank increases. The increase is very rapid for coals having carbon content of 85 percent or higher. Medium volatile bituminous coking coal having high free swelling index (≥ 4) possesses graphitizing carbon and ultimately produces a crystalline structure of graphite at 2700°C.

Keywords : Coal, graphitic carbon, X-ray diffraction.

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The study of carbons as a precursor to graphite is of enormous theoretical and technological importance in electrical, chemical, metallurgical and nuclear fields. The main source of carbon is coal. Generally, the carbons are classified into two groups namely, graphitizing and non-graphitizing carbon [1]. Graphitizing carbons are relatively soft [2], high apparent density, rich in hydrogen, or low in oxygen, nitrogen and sulfur and possess low microporosity. Non-graphitizing carbons are generally hard [2], low apparent density, high microporosity and are relatively low in hydrogen or rich in oxygen, nitrogen and sulfur.

The structure of graphite [3] consists of extensive parallel layers of carbon atoms arranged in condensed aromatic ring arrays, the layers being mutually oriented and separated by a distance of 0.335 nm (the carbon-carbon van der Walls' distance). The parallel stacking of layers in coal is similar to graphite, but lacks in mutual oricntation between layers, and the average spacing between layers is somewhat larger.

All low-rank coals belong to the class of non-graphitizing carbon because of less number of aromatic ring compounds present in the coal and its structure is strongly cross-linked. But higher-rank coals belong to the class of graphitizing carbon and they pass through a plastic stage during carbonization [4]. With a few exception, these coals fall in the bituminous range of medium volatile coal. A coal with a free swelling index of ≥ 4 may have good coking properties [5].

X-ray diffraction studies of coal have been carried out by a number of workers [6–8]. In most cases, the diffraction patterns were obtained with two or more diffuse peaks at the positions of the most prominent graphitic peaks. The recent X-ray work by Diamond [9], adds more details to the picture of the carbonization process. During carbonization, coals undergo some bond breaking reactions and reduction of hydrogen bonding, some molecular rearrangement, condensation reactions and molecular stripping takes place. The presence of sulfur in coal causes the cross linking in between the parallel layers. Up to 500°C, a relatively high proportion of 'Disordered' material is lost, probably including hydroxyl and aliphatic groups, allowing the layers to align in parallel arrays to have a sharp peak.

The present paper is concerned about the study of graphitic carbons in Bangladeshi bituminous coal which is discovered recently in the Northwestern part of the country.

High-rank, medium-volatile (having range of 21 to 25 daf%) bituminous coals of Khalaspir Northwestern Bangladesh [10,11] were taken to study its graphitization The coals were heat-treated at 1000°C for 2 hours under oxygen free nitrogen in a laboratory tube furnace to produce coke, and then samples of this coke were heated subsequently to high temperature by four steps, 1300°C, 1900°C, 2200°C for a short interval of time in each step and finally at 2700°C for 2 hours in a graphitization furnace in an argon atmosphere.

Elemental analyses were carried out as per ASTM D3176 [12] by Carlo Erba Elemental Analyzer model no 1106, made by M/S Carlo Erba Strumentazione, Milan, Italy. The test for the free swelling index of coals was performed as per ASTM D720 [12]. Coal samples were crushed into fine powder using mortar and pestle and then powder was sieved through 200 mesh. X-ray powder diffraction was carried out using a two circle diffractometer (made by Seifert & Co, Germany, Seifert XRD 3000 P) with Cu Kα radiation at 30 mA/35 KV. The wavelength of the X-ray radiation was 1.5418 Å.

An elemental analyses of the coals are presented in Table 1. The elemental analysis reveals that coal lies in the higher rank of bituminous type. The coal also contains very low sulfur and it appears to have less cross-linking and dehydrogenation in the decomposing material resulting in a graphitizing carbon. Figure 1 contains the diffraction patterns of four coal samples showing an increase in sharpness of the diffraction lines with increasing carbon content. The interlayer distances of different coal samples calculated from Figure 1, are also depicted in Table 1. It is seen that the interplanar distance decreases with increasing

Table 1. Elemental analysis and calculation of interlayer spacings.

Samples	Elemental analysis, wt% daf*						*d* values for three reflections		
	C%	H%	O%	N%	S%	FSI	(002)	(100)	(004)
Natural graphite	100						3.326	2.127	1.700
Graphitized coking coal at 2700°C/2 hrs.	100						3.373	–	1.711
Coal, GDH-46, Depth-375.5 m	89.67	5.55	1.82	1 97	0.99	7.5	6.941	3.329	1.785
Coal, GDH-46, Depth-350.2 m	86.64	5.66	6.67	traces	1.03	7.0	7.212	3.367	1 795
Coal, GDH-45, Depth-301 4 m	85.77	5 16	6.39	1 83	0.85	7.5	7.352	3.537	1.80
Coal, GDH-45, Depth-402 9 m	81.75	6.13	10 27	1.45	0.40	6.5	7.558	3.812	1.83

*Daf : Dry ash free; FSI · Free swelling index; GDH · Geological drilling hole.

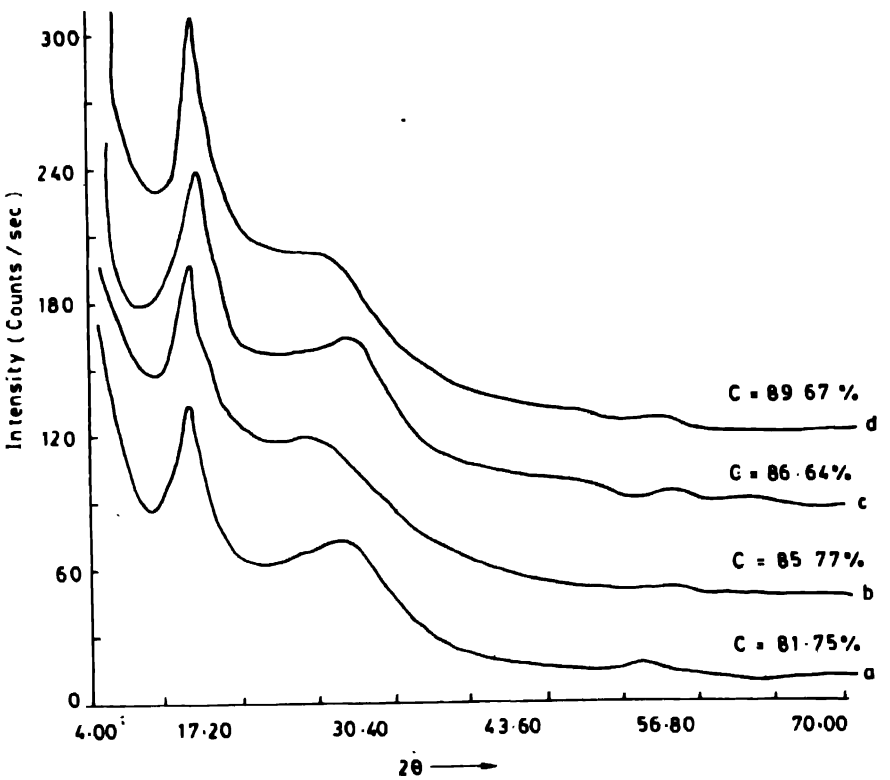

Figure 1. X-ray diffractograms of the coalification process of Khalaspir coal. (a) GDH-45, Depth-402.9 m; (b) GDH-45, Depth-301.4 m, (c) GDH-46, Depth-350.2 m; (d) GDH-46, Depth-375.5 m. For convenience, diffractograms represented by b, c and d are shifted upwards by 50 cps along Y axis.

carbon content. It is believed that broadened peaks are caused due to the formation of small crystallites. As coal is a poor crystalline material and mixed with mineral matter, it contains a cluster of some hexagonal ring compounds. The structural arrangement of coal increases upto the formation of organic macromolecules of flat shape with the increase of coal rank as well as with the increase of carbon content. The carbon hexagons are considered to be embryos of the graphite arrangement. Every macromolecule has several carbon hexagons, which make up a planar pattern. At the higher stages of coalification, the carbon embryos arrange themselves into parallel positions and come closer, leading ultimately to a regular periodicity in the vertical direction. So with increasing coalification, the interplanar spacing of carbon hexagonal planes decreases and approaches a regular crystalline structure to that of graphite. For pure crystalline graphite, sharp peaks are found for (002), (100), (101), (102), (004) planes. In case of the present coal samples, a diffraction peak for (002) plane is observed, which is found to increase in sharpness with the increase of carbon content *i.e.* with increased crystallinity. X-ray diffraction pattern of natural graphite (supplied by Carbon Tech. Unit, National Physical Laboratory, New Delhi, India) is shown in Figure 2.

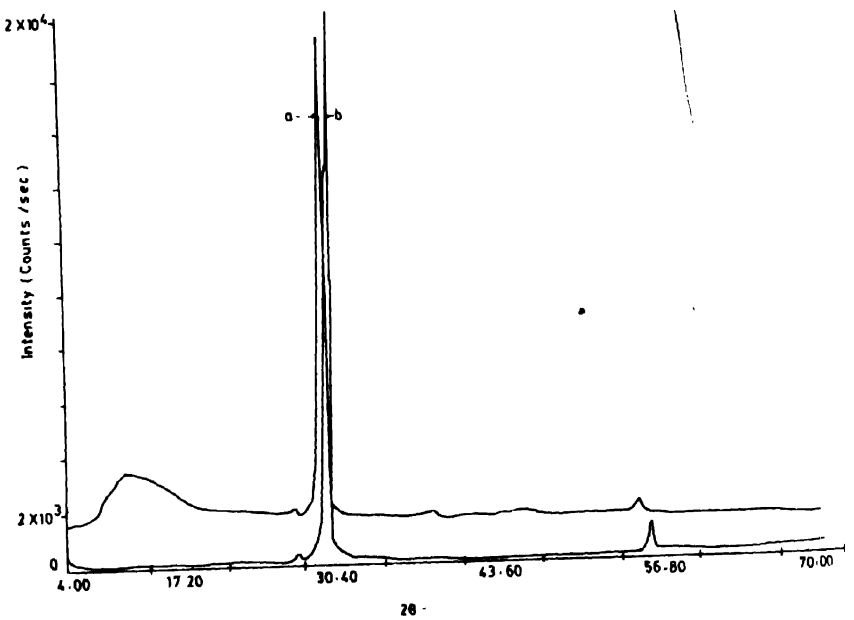

Figure 2. X-ray diffractograms of graphite : (a) Synthetic graphite derived from coal of GDH-46, Depth-375.5 m heat treated at 2700°C for 2 hours; (b) Natural graphite.

where the interlayer distance (c/2) is 3.326 Å and 1.709 Å for (002) and (004) reflections respectively. Figure 2 shows X-ray diffraction pattern of coal after graphitization at 2700°C for 2 hrs under argon flow. The interlayer distance (c/2) is found to be 3.373 Å and 1.711 Å for (002) and (004) reflections respectively, which resemble the corresponding values of graphite structure.

The following conclusions on graphitizing coal can be drawn :

(1) The coal should be of higher rank of bituminous and medium volatile type having low ash and low sulfur content.

(2) The coal should be coking type and free swelling index value should be greater than ≥ 4. They should have to pass through a plastic or liquid state (*i.e.* mesophase transition) in low temperature carbonization.

(3) During high temperature carbonization the interlayer distance should be decreased. To summarize, Khalaspir coals of Northwestern Bangladesh follows the above criteria of graphitizing coal.

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